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PATENT SPECIFICATION

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(54) IMPROVEMENTS IN SHEET MATERIALS

- (71) We, CELANESE CORPORATION, of 522 Fifth Avenue, New York 36, State of New York, United States of America, a company incorporated in accordance with the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to improvements in porous sheet materials.
- The specification of our prior Patent No. 1,143,474 describes *inter alia* the production from a polymer exhibiting crystallinity of films of lower density than that of films normally obtained by extrusion of a liquid consisting of or containing the polymer; such films contain voids of less than 5000 Angstrom units diameter which are accessible to the outside surfaces of the films which are thus of the so-called open-celled structure and are porous. Our later Patent No. 1,180,066 and our co-pending Applications Nos. 54056/70 (1,287,504) and 54057/70 (1,287,505) describe modifications in such microporous films and their production.
- Microporous films of the kind referred to are eminently suitable for use as "breathable" medical dressings, i.e. dressings which are readily permeable to gases and vapours but not to liquids. However, they do not possess as high a strength as is needed for some uses to which they might otherwise be put, for instance, sterile packaging or hospital bed covers.
- The present invention is concerned with a composite product embodying a microporous film of the kind referred to and retaining the minute pores by which the microporous film is characterised but possessing substantially greater strength.
- The composite structure of the invention comprises a microporous polymer film in which the polymer has a crystallinity of at least 30%, which film has been drawn to exhibit molecular orientation and is of lower bulk density than a film of the same polymer not having an open-celled structure and has a surface area per cc. of 2 to 200 square metres, elongated and substantially parallel interconnected non-porous surface regions separating porous surface regions comprising a plurality of fibrils, which fibrils are randomly disposed throughout each porous region, are substantially parallel to each other and to the direction of molecular orientation and define pore spaces of 100 to 5000 Angstrom units, said pore spaces forming tortuous paths between the two surfaces of the film to endow the film with a porosity volume per gram of from 0.05 to 1.5 ccs. and a Q value (as hereinafter defined) of 5 to 400, the microporous film being united surface to surface with a macroporous sheet having an average pore size of at least 5 microns and an open space area amounting to 1 to 50% of the overall area of the sheet.
- It will be appreciated that the microporous film used according to the invention is analogous to a film such as is described in our

co-pending Application No. 54057/70 (1,287,505) and the terms used in defining it are those used in that Application; thus, the term "bulk density" as used in the description and claims of the present Application means the weight per unit of gross volume of the film as determined by immersing a known weight of the film in a graduated vessel partly filled with mercury at 25°C and atmospheric pressure, the rise in the level of mercury giving a direct measure of the gross volume.

The production of the microporous polymer film from a non-porous film of a crystalline, elastic polymer may be by the process described in our Application No. 54057/70 (1,287,505) which includes cold drawing the elastic film until porous surface regions or areas which are elongated perpendicular to the stretch direction are formed, hot drawing the cold stretched film until fibrils and pores or open cells which are elongated parallel to the stretch direction are formed and thereafter heat setting the resulting porous film under tension at substantially constant length to impart stability to the film.

The essence of this process is the discovery that the sequential cold stretching and hot stretching steps impart to the elastic film a unique open-celled structure which results in advantageous properties, including improved porosity, improved thermal stability and a gain or enhancement of porosity when treated with certain organic liquids such as perchloroethylene. Microporous films can thus be obtained which have a greater proportion of surface area covered by the pores, a greater number of pores and a more uniform distribution of pores, than is the case with microporous films obtained by prior processes. Moreover, the fibrils present in the films are more highly drawn than the rest of the polymer material in the film and thus contribute to the higher thermal stability of the film.

The total surface area per cubic centimetre of material of the films used in the present invention is preferably from 5 to 100 square metres and especially from 10 to 80 square

metres. These values can be compared with a pin-punched film which has a total surface area per gram of 0.1 square metres; paper and fabric which have values per gram of 1.0 square metres and leather which has a value of 1.6 square metres per cc. The volume of space per weight of material preferably ranges from 0.1 to 1.0 cubic centimetres per gram and especially from 0.2 to 0.85 cubic centimetres per gram. The microporous films preferably have a nitrogen Flux value (Q value) in the range of from 50 to 300; the Q value is determined by mounting a film sample having a surface area of 6.5 square centimetres in a membrane cell having a volume of 63 cubic centimetres, applying to the cell a differential pressure (the pressure drop across the film) of 200 pounds per square inch with nitrogen, stopping the supply of nitrogen and noting the time required for the pressure to drop to a differential pressure of 150 pounds per square inch as the nitrogen permeates through the film. The Q value, in gram moles per square centimetre minute $\times 10^3$, is then determined from the equation

$$Q = \frac{27.74 \times 10^3}{t \times T}$$

where t is the elapsed time in seconds and T is the temperature of nitrogen in degrees Kelvin. The above equation is derived from the gas law, $PV = ZnRT$.

The microporous films are desirably formed from elastic films of crystalline polymers, the elastic films having an elastic recovery at zero recovery time when subjected to a standard strain of 50 per cent, at 25°C and 65 per cent relative humidity, of at least 40 per cent, preferably at least 50 per cent and especially at least 80 per cent.

Elastic recovery (EA), as used herein, is a measure of the ability of a film to return to its original size after being stretched and is calculated from the formula

$$ER\% = \frac{\frac{\text{(total length when stretched)}}{\text{length added when stretched}} - \frac{\text{(length after stretching and relaxing)}}{\text{length added when stretched}}}{\text{length added when stretched}} \times 100$$

Although a standard strain of 50 per cent is used to identify the elastic properties of the starting films such starting films, in general, have elastic recoveries higher at strains less than 50 per cent, and somewhat lower at strains substantially higher than 50 per cent, as compared with their elastic recovery at a 50 per cent strain.

The starting elastic films have a per cent crystallinity of at least 30 per cent and, especially, at least 50 per cent, e.g. 50 to 90 per cent. Per cent crystallinity is determined

by the x-ray method described by R. G. Quynn et al in the Journal of Applied Polymer Science, Volume 2, No. 5, pages 166 to 173 (1959).

Preferred starting elastic films and their preparation are described in our British Patent No. 1,198,695 and our co-pending Applications Nos. 54056/70 (1,287,504) and 54057/70 (1,287,505). Other elastic films which are suitable are described in British Patent No. 1,052,550.

The starting elastic films employed are

made from a polymer of a type capable of developing a significant degree of crystallinity, as contrasted with classical elastic materials, such as the natural and synthetic rubbers, which are substantially amorphous in their unstretched or tensionless state. An important group of polymers from which the starting films may be made consists of the olefine polymers, e.g. polyethylene, polypropylene, poly-3-methyl butene-1, poly-4-methyl pentene-1, as well as copolymers of propylene, 3-methyl butene-1, 4-methyl pentene-1, or ethylene with each other or with minor amounts of other olefines, e.g. copolymers of propylene and ethylene, copolymers of a major amount of 3-methyl butene-1 and a minor amount of a straight chain n-alkene such as n-octene-1, n-hexadecene-1, n-octadecene or other relatively long chain alkenes, as well as copolymers of 3-methyl pentene-1 and any of the same n-alkenes mentioned previously in connection with 3-methyl butene-1.

When a propylene homopolymer is used it is preferably an isotactic polypropylene having a per cent crystallinity as indicated above, a weight average molecular weight ranging from 100,000 to 750,000, preferably 200,000 to 500,000, and a melt index (ASTM-1958D-1238-57T, Part 9, page 38) from 0.1 to 75, preferably 0.5 to 30.

While the invention will be described more particularly in connection with films of olefine polymers, it may be applied also to, for instance, films of high molecular weight oxymethylene polymers, including both homopolymers and copolymers, the preferred polymer being a "random" oxymethylene copolymer which contains recurring oxymethylene units interspersed with —OR— groups in the main polymer chain, where R is a divalent radical containing at least two carbon atoms directly linked to each other and positioned in the chain between the two valences free from any substituent functional groups which would induce undesirable reactions, and wherein a major amount of the —OR— units exist as single units attached to oxymethylene groups on each side. Examples of preferred polymers include copolymers of trioxane and cyclic ethers continuing at least two adjacent carbon atoms such as the copolymers disclosed in British Patent No. 903668. These polymers in film form may also commonly have a crystallinity of at least 50 per cent, e.g. 50 to 60 per cent, melting points of at least 150°C and number average molecular weights of at least 10,000.

Other polymers from which the starting film may be made are the polyalkylene sulphides, e.g. polymethylene sulphide and polyethylene sulphide, the polyarylene oxides, e.g. polyphenylene oxide, the polyamides, e.g. polyhexamethylene adipamide (nylon 66) and polycaprolactam (nylon 6), and polyesters, e.g. polyethylene terephthalate.

Conventional film-forming apparatus may be used for forming the starting elastic films, for example a film extruder equipped with a shallow channel metering screw and coat hanger die is satisfactory. Generally, the polymer is introduced into a hopper of the extruder which contains a screw and a jacket fitted with heating elements. The polymer is melted and transferred by the screw to the die from which it is extruded as a film through a slot from which it is drawn by a take-up or casting roll. The die opening or slot width may be in the range of, for example, from 10 to 200 mils.

Using this type of apparatus, film may be extruded at a draw-down ratio of 20:1 to 200:1, preferably 50:1 to 150:1. The term "draw-down ratio" or, more simply, "draw ratio", as used herein is the ratio of the film wind-up or take-up speed to the speed of the film issuing at the extrusion die.

The melt temperature for film extrusion is, in general, no higher than 100°C above the melting point of the polymer and no lower than 10°C above the melting point of the polymer. For example, polypropylene may be extruded at a melt temperature of 180°C to 270°C, preferably 200°C to 240°C, polyethylene may be extruded at a melt temperature of 175°C to 225°C, while oxymethylene polymers, e.g. those of the type disclosed in British Patent No. 903668, may be extruded at a melt temperature of 185°C to 235°C, preferably 195°C to 215°C.

The extrusion operation is preferably carried out with rapid cooling and rapid draw-down in order to obtain maximum elasticity. This may be accomplished by having the take-up roll relatively close to the extrusion slot, e.g. within two inches and, preferably, within one inch. An "air knife" operating at temperatures between, for example, 0°C and 40°C may be employed within one inch of the slot to cool and solidify the film quickly. The take-up roll may be rotated at a speed of, for example, 10 to 100 ft/min., preferably 50 to 500 ft/min.

The starting film may also be made by the well known blown film extrusion method in which the molten polymer enters a die from which it is extruded through a circular slot to form a tubular film having an initial diameter D_1 and is blown up to a diameter D_2 . Using this method, the draw-down ratio is preferably 20:1 to 200:1, the slot opening 10 to 200 mils, the D_2/D_1 ratio 0.5 to 6.0, preferably 1.0 to 2.5, and the take-up speed 30 to 700 ft/min.

The extruded film may then be initially heat treated or annealed in order to improve its crystal structure, e.g. by increasing the size of the crystallites and removing imperfections therein, before being subjected to the consecutive steps of cold stretching, hot stretching and heat setting.

The term "cold stretching" as used herein means stretching a film to greater than its original length while it is at a temperature below that at which melting of the film begins when the film is uniformly heated from a temperature of 25°C at a rate of 20°C per minute. The term "hot stretching" as used herein means stretching at above the temperature at which melting begins when the film is heated from a temperature of 25°C at a rate of 20°C per minute, but below the normal melting point of the polymer, i.e. below the temperature at which fusion occurs. For example, using polypropylene elastic film, cold stretching is carried out preferably below 120°C while hot stretching is carried out above this temperature.

The heat setting step is carried out at from 125°C up to a temperature below the fusion temperature of the film in question. For polypropylene the range is preferably 130°C to 160°C.

The resulting microporous film exhibits a final crystallinity of at least 30 per cent and, preferably, 50 to 100 per cent, as determined by the x-ray method, and an average pore size of 100 to 5000 Angstrom units, usually 150 to 3000 Angstrom units, as determined by mercury porosimetry as described in an article by R. G. Quynn, on pages 21 to 34 of Textile Research Journal, January 1963.

The macroporous sheet used in the process of the invention may be a plastics film or a non-woven or woven material having an average pore size of at least 5 microns, (50,000 Angstrom Units) and preferably above 50 microns, e.g. 75 microns or higher. Preferably the macroporous sheet has from 5 per cent to 25 per cent open area. The open area or macropores may be achieved by any desired means, for instance by forming the sheet by conventional processes for making non-wovens and woven materials, but the most convenient technique is to use a simple pin punch on a plastics film.

The macroporous sheet may be united to the microporous film by any desired means. A thin coating of pressure sensitive adhesive may be applied to one of the surfaces to be joined and the two surfaces then pressed together. Great care should, however, be exercised when this method is employed, as too thick a coating of adhesive will cover the pores in the microporous film and reduce or destroy its permeability. In this regard, it has been found that where pressure sensitive adhesives are employed, it is best to employ the technique of spraying the adhesive so as to deposit only a relatively thin film. Other techniques may be employed such as coating a solution of an adhesive on to the non-stretched precursor film used for making the microporous film and subsequently stretching it so as to form an adhesive microporous structure.

The use of a heated embossing roll will effect union of the film and sheet without the use of an adhesive. In some end uses, such as surgical applications, embossing technique is the preferred method for forming the laminate to eliminate the unnecessary inclusion of unwanted chemicals that could cause irritation to the human skin.

In the embossing method, however, since heat is employed, a further restriction must be placed upon the physical properties of the macroporous sheet. If the macroporous sheet had a higher softening temperature than the microporous film, the micropores would disappear before any bonding took place. Accordingly, the macroporous sheet should have a softening temperature similar to, or at least not greater than, the softening temperature of the microporous film. Preferably, when the embossing technique is employed, the softening temperature of the macroporous sheet does not in any case exceed 160°C. Of course, if, for instance, the microporous film has a softening temperature of 125°C, this is the upper limit of softening temperature for any macroporous sheet if the embossing technique is employed. Furthermore, it is clear that the temperature of the embossing roll should not exceed the softening temperature of either the macroporous sheet or the microporous film; preferably the roll temperature is approximately 5°C lower than the softening temperature of the microporous film.

The composite structure of the invention, besides being strong enough for such uses as sterile packaging material or hospital bed covers, is remarkable for its high degree of porosity since a much greater proportion of the porosity of the microporous film is retained than would be expected when the open area of the macroporous sheet is considered. This is brought out in the following Examples which illustrate the invention.

EXAMPLES I—VI

Microporous polypropylene film having a total surface area of 80 square meters per cc., a volume of space per weight of material of 0.5 cubic centimeters per gram and a Q flux value of 113 was contacted with polypropylene film which had been pin punched with holes 0.045 inch in diameter with a metal die punch spiked roller. The microporous polypropylene film and the pin punched polypropylene film were then put through an embossing roll revolving at 8 revolutions per minute at 80°C. and a pressure of 250 pounds per square inch. The physical properties of the resultant product is compared with the above described microporous polypropylene film with no macroporous backing in Table I.

The pore-size of the microporous films in Examples I—VI was somewhat less than 5000 Angstrom units, and the crystallinity was greater than 30%. The average pore size of the

macroporous sheet, in Examples I—VI as well as in Examples VII and VIII ranged from 5—1000 microns; where the pores were formed by pin punching the size of each pore in accordance with the invention.

TABLE I

Example	Percent Open Area on Pin Punched Film	Permeability ^F Gurley	MVTR ^G	Tear ^H M.D.	Elmendorf ^I M.D.	Mullen ^J Burst
Base micro-porous polypropylene film standard		30	1700	1.2	2	16
I	36 ^A	42	1540	1.8	42	33
II	27 ^B	43	1240	2.0	55	36
III	0	not permeable		2.1		
IV	9.5 ^C	47		1.8		
V	18 ^D	41		1.5		
VI	1 ^E	80	730	1.4		

A) 36 percent open area contains 225 holes per square inch.

B) 27 percent open area contains 168 holes per square inch.

C) 9.5 percent open area contains 60 holes per square inch.

D) 18 percent open area contains 112 holes per square inch.

E) 1 percent open area contains 7 holes per square inch.

F) measured in seconds (10) per cubic centimeter per ASTM D—7265A

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TABLE I (continued)

G) measured in grams per 24 hours square meters per ASTM E-96-66

H) measured in pounds per ASTM D-1004-61

I) measured in grams per ASTM D-1922-67

J) measured in pints per ASTM D-774-63.

EXAMPLE VII.

The microporous polypropylene film employed in Examples I to VI was contacted with a Kimton-Kendall viscose rayon non-woven fabric. The microporous film and the non-woven fabric were laminated by means of a vinyl acetate-maleate adhesive emulsion containing fifty-six weight percent solids. The resulting laminated exhibited a Gurley reading of 45 seconds per 10 cubic centimeters and a moisture vapor transmission reading of 1350 grams per 24 hours square meters.

EXAMPLE VIII.

The microporous polypropylene film employed in Examples I to VII was contacted with a Texwipe woven cloth (available from the Texwipe Company's Hillsdale, New Jersey). The microporous film and the woven material were laminated by means of a vinyl acetate-maleate adhesive emulsion containing fifty-six weight percent solids. The resulting laminate exhibited a Gurley reading of 80 seconds per 10 cubic centimeters and a moisture vapor transmission reading of 730 grams per 24 hours square meters.

In like manner other plastics of similar softening temperature as the microporous polypropylene were utilized employing the embossing technique (e.g. polyethylene and ethylene/vinyl acetate copolymer) with equally good results. The beneficial results were greatly diluted when a polymer of vastly

dissimilar softening temperature was employed (e.g. polyethylene terephthalate). This relatively inferior result can be obviated in either of two manners. Initially, a microporous polyethylene terephthalate film can be embossed to a microporous polyethylene terephthalate film with enhanced results. Secondly a base polypropylene microporous film may be united to a microporous polyethylene terephthalate film by means of an adhesive instead of using the embossing technique. To further demonstrate the value of the invention other microporous films were employed (e.g. polyethylene and polyacetal) and gave satisfactory results.

WHAT WE CLAIM IS:—

1. A porous composite structure which comprises a microporous polymer film in which the polymer has a crystallinity of at least 30%, which film has been drawn to exhibit molecular orientation and is of lower bulk density than a film of the same polymer not having an open-celled structure and has a surface area per cc. of 2 to 200 square metres, elongated and substantially parallel interconnected non-porous surface regions separating porous surface regions comprising a plurality of fibrils, which fibrils are randomly disposed throughout each porous region, are substantially parallel to each other and to the direction of molecular orientation and define pore spaces of 100 to 5000 Angstrom units, said pore spaces forming tortuous paths between the two surfaces of the film to endow

- the film with a porosity volume per gram of from 0.05 to 1.5 ccs. and a Q value (as hereinbefore defined) of 5 to 400, the microporous film being united surface to surface with a macroporous sheet having an average pore size of at least 5 microns and an open area amounting to 1 to 50% of the overall area of the sheet.
- 5 2. A porous composite structure according to Claim 1, wherein the microporous film is made of polypropylene.
- 10 3. A porous composite structure according to Claim 1 or 2, wherein the macroporous sheet is thermoplastic and softens at substantially the same temperature as the microporous film.
- 15 4. A porous composite structure according to Claims 2 and 3, wherein both the microporous film and the macroporous sheet are made of polypropylene.
- 20 5. A porous composite structure according to any of the preceding claims, wherein the macroporous sheet is a pin punched film.
- 25 6. A porous composite structure according to any of the preceding claims, wherein the open surface area of the macroporous sheet is from 5 to 25 per cent of its total surface area.
7. A porous composite structure according to any of the preceding claims in which the film and the sheet are united by being embossed.
- 30 8. A porous composite structure substantially as hereinbefore described.
9. A process for the production of a porous composite structure as claimed in Claim 7, which comprises pressing the microporous film and the macroporous sheet together by means of an embossing roll heated to a temperature not higher than 5°C below the softening temperature of the microporous film.
- 35 40 10. Process for the production of a porous composite structure substantially as hereinbefore described.

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